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character from the observed value of the dipole moment. It has been shown by Robinson[29] that even in so simple a molecule as HCl the large contribution to the dipole moment by purely covalent structures and the sensitivity of this contribution to hybridization of bonding orbitals renders attempts at simple correlation of dipole moment and ionic character of doubtful value. *A fortiori*, attempts at detailed correlation of the dipole moment of a polyatomic molecule with properties of a bond in the molecule must be viewed with great scepticism. However, it seems likely that in a rough, qualitative fashion, the marked reduction in the dipole moment observed for the silicon compounds is a result of the importance of double bond structures for these molecules.

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[29] D. Z. Robinson, J. Chem. Phys. **17**, 1022 (1949).

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# The Molecular Structure of Cyclobutane

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The cyclobutane molecule has been found by electron diffraction to have the following bond distances and bond angles: C−C, $1.56_8 \pm 0.02$A; C−H, $1.09_6 \pm 0.04$A; ∠HCH, $114 \pm 8°$. On the average the ring is nonplanar, with dihedral angle 20° (+10°, −20°), but the equilibrium symmetry may be either $D_{2d}$ (puckered ring) or $D_{4h}$ (planar ring with low rigidity leading to large amplitude of out-of-plane bending). This point is discussed in connection with earlier spectroscopic work. The long bond distances found in four-membered rings are contrasted against the short distances in three-membered rings, and the strain energies, bond distances, and HCH angles of cycloalkanes are discussed in terms of modern valence concepts. It is suggested that the potential energy arising from a repulsion of the nonbonded carbon atoms may contribute significantly to the apparently anomalously high strain energy of cyclobutane. The repulsive force associated with such a potential is shown to account satisfactorily for the long C−C distances.

RECENT structure analyses of cyclobutane derivatives provide evidence that the carbon-carbon single bonds in 4-membered rings are longer than 1.54A, the standard distance. Reported values are 1.55 ±0.02A and 1.56±0.03A for methylenecyclobutane,[1,2] 1.56±0.05A for dimethyl ketene dimer,[3] 1.555 and 1.585 (both ±0.02A) for tetraphenylcyclobutane,[4] 1.60A for octafluorocyclobutane,[5] and 1.59A for octachlorocyclobutane;[6] in dinaphthylenecyclobutane[7] the distances projected onto a crystal plane are 1.56A and 1.60A. In tetraphenylcyclobutane and dinaphthylenecyclobutane the 4-membered ring is centrosymmetric and therefore planar, but in the octafluoro and octachloro derivatives the ring appears to be definitely puckered. We have undertaken the present electron diffraction investigation in order to determine the structure of the parent hydrocarbon cyclobutane.

## EXPERIMENTAL

Our sample was kindly supplied from the Chemical Laboratories of the University of California by Professor K. S. Pitzer, and the electron diffraction photographs were taken using the apparatus described by Brockway.[8] Visual examinations of the photographs were made by both of us, independently and also in consort, and we believe that the reduced intensity curve is represented by Fig. 1 ($V$) subject to certain modifications.[9]

The radical distribution curve (Fig. 1, $R$), calculated

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† Contribution No. 1691.

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[4] J. D. Dunitz, Acta Cryst. **2**, 1 (1949).

[5] H. P. Lemaire and R. L. Livingston, J. Chem. Phys. **18**, 569 (1950).

[6] T. B. Owen and J. L. Hoard, Acta Cryst. **4**, 172 (1951).

[7] J. D. Dunitz, XIIth International Congress of Pure and Applied Chemistry, New York, 1951.

[8] L. O. Brockway, Revs. Modern Phys. **8**, 231 (1936). Camera distance, 10.95 cm. Wavelength, 0.06082 A, determined from ZnO photographs (C. S. Lu and E. W. Malmberg, Rev. Sci. Instr. **14**, 271 (1943): $a=3.2492$ A, $c=5.20353$ A). Corrections were made for film expansion.

[9] The curve is based on J. D. D.'s original interpretation of the photographs and was used for the radial distribution calculation. In showing the 3rd, 4th, 6th, and 7th maxima equally intense, it differs slightly from V. S.'s interpretation, which makes the 4th maximum slightly stronger and the 6th slightly weaker than the average of these features. It happens, also, that the nature of the fifth ring (shoulder) as indicated by both our original sketches is better represented by theoretical curves $B$ and $D$ than by $V$.

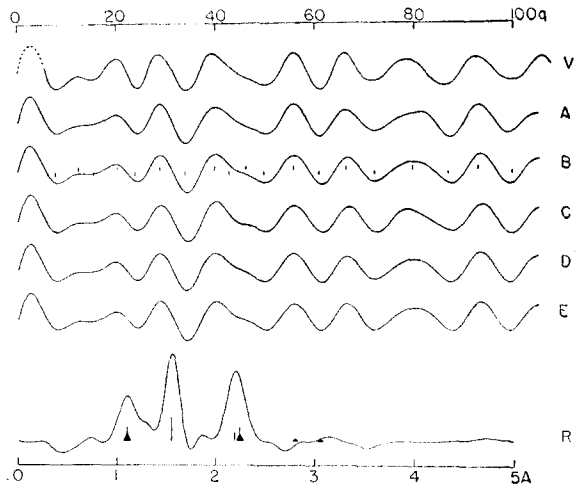


FIG. 1. Electron diffraction curves for cyclobutane, $C_4H_3$. *V*, visual curve. (The dotted portion is drawn in accordance with the theoretical curves.) *A–E*, theoretical curves.

| Model | C−C (A) | C−H (A) | ∠HCH (°) | Dihedral angle (°) |
|---|---|---|---|---|
| *A* | 1.56 | 1.10 | 116 | 0 |
| *B* | 1.56 | 1.10 | 116½ | 22 |
| *C* | 1.56 | 1.10 | 117 | 33 |
| *D* | 1.56 | 1.10 | 112 | 22 |
| *E* | 1.56 | 1.08 | 113½ | 22 |

*R*. Radial distribution curve from *V*.

with the equation[10,11]

$$rD(r)=\sum_{q=1,2\cdots}^{q\,\max} I(q)\exp(-aq^2)\sin\frac{\pi}{10}qr$$

with $\exp[-a(100)^2]=0.1$, has maxima at 1.11 A (C−H), 1.56 A (C−C), and 2.21 A (nonbonded C···C and shorter nonbonded C···H). No peaks corresponding to longer C···H distances appear.

The theoretical intensity curves were calculated with the simplified scattering formula[10]

$$I(q)=\sum_{i,j}\frac{Z_iZ_j}{r_{ij}}\exp(-b_{ij}q^2)\sin\left(\frac{\pi}{10}r_{ij}q\right)$$

with $b_{ij}$ equal to 0.00016 for bonded C−H, 0.0003 for unbonded C···H,[12] and zero for C−C and C···C terms. An effective value, 1.25, was taken for $Z_H$. All $H\cdots H$ terms were omitted.

Models of symmetry $D_{4h}$ were first examined over a reasonable range of the shape parameters, $\rho=1.56$ C−H/C−C and ∠HCH, but none was found completely satisfactory. Closest agreement with our observations is given by the model with $\rho=1.10$ and ∠HCH = 116° (Curve *A*), which was chosen as starting point for models of the lower symmetry $D_{2d}$. For these, the local $C_{2v}$ symmetry of the $>CH_2$ groups was retained. A 22° dihedral angle between opposite triads of carbon atoms then leads to almost complete accord with our observations (Curve *B*); increase of the angle to 33° (Curve *C*) introduces certain disagreements, perhaps worse than those with angle 0°. Finally, the values of $\rho$ and ∠HCH were readjusted somewhat in accordance with a strict adherence to the fine details of our interpretation of the appearance of the photographs. Quantitative comparison of measured and calculated $q$ values for three models which agree almost equally well with our observations leads (Table I) to the final parameter values and limits of error, $C-C=1.56_8\pm0.02$A, $C-H=1.09_6\pm0.04$A, $\angle HCH=114\pm8°$, and dihedral angle $=20°(+10°,-20°)$.

Consideration of the frequency of the totally symmetric C−H stretching vibration in cyclobutane[13] (2937 $cm^{-1}$) together with the C−H distances and corresponding frequencies in methane[14] (1.093A, 2914 $cm^{-1}$) and ethane (1.102A,[15] 2899 $cm^{-1}$)[16] makes it unlikely that our estimate of the C−H distance in cyclobutane is actually in error by more than 0.01A. The assumption of this limit of error would reduce the uncertainty of the ∠HCH determination by about 2°.

Our result shows that the cyclobutane ring is nonplanar, but we are unable to distinguish between static nonplanarity (symmetry $D_{2d}$) and dynamic nonplanarity (symmetry $D_{4h}$ with large amplitude of out-of-plane ring bending.) Wilson,[13] on spectroscopic evidence, has assigned the symmetry $D_{4h}$ to the molecule and a frequency 145 $cm^{-1}$ to the out-of-plane bending vibration. With this frequency and the assumption of harmonicity we expect[17] a measurement of the root-mean-square dihedral angle to give a value of about 15°. Wilson, however, considered an incorrect point group ($C_{2v}$) for the nonplanar model so that his conclusions, although not inconsistent with the electron diffraction evidence, are questionable; the reported infrared and Raman frequencies appear to agree at least as well with $D_{2d}$ as with $D_{4h}$ selection rules. Further spectroscopic work is obviously required for the establishment of the correct molecular symmetry.

## DISCUSSION

The present analysis provides a further example of the lengthening of carbon-carbon bonds in four-mem-

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[11] Shaffer, Schomaker, and Pauling, J. Chem. Phys. **14**, 659 (1946).
[12] Some additional curves were calculated with a larger value of $b_{ij}$ for the longer unbonded C···H terms, but the resulting changes were insignificant.
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[14] D. M. Dennison, Revs. Modern Phys. **12**, 175 (1940).
[15] G. E. Hansen and D. M. Dennison, J. Chem. Phys. **20**, 313 (1952).
[16] G. Herzberg, *Molecular Spectra and Molecular Structure*, (D. Van Nostrand Company, Inc., New York, 1945), Vol. II, p. 345.
[17] In the expression $\overline{x^2}=h\coth(h\nu/2kT)/8\pi^2\mu\nu$ for the mean-square displacement of a harmonic oscillator, we have taken $\mu=17$ rather than $\mu=14$ for the system, composed of two pairs of $CH_2$ groups, to allow for the greater amplitude of the hydrogen atoms compared with carbon.

bered rings. The lengthening is all the more striking if these bond distances are compared not only with the standard value 1.54A but also with the short distances reported for three-membered rings. In cyclopropane, the C−C distance has been reported as 1.53±0.03A,[18] 1.54A,[19] and 1.515±0.02A;[20] in the highly strained spiropentane molecule[21] the average distance is 1.49 ±0.01A, the central bonds, subject to the greatest strain, being somewhat shorter than the peripheral bonds; 1.473A has been found for the C−C distance in ethylene oxide;[22] and in cyclopropene[23] the distances are 1.286±0.04A for the double bond, also shorter than normal, and 1.525±0.02A for the single bonds. The experimental evidence thus indicates that the C−C distance is lengthened in four-membered rings, but is shortened in three-membered rings. The HCH angles in these strained molecules are significantly larger than tetrahedral, the reported values being 114° for cyclobutane, 118°[19] and 116°[20] for cyclopropane, 117° for ethylene oxide, and 120° for spiropentane. (We shall not attempt to discuss the notably lesser widening, in corresponding substituted molecules, of peripheral bond angles HCX and XCX, with X not equal to H, from their normal values.) The empirical strain energies are, of course, also of interest, and recent values for theh eats of combustion of cyclopropane[24] (499.9 kcal mole$^{-1}$), cyclobutane[25] (655.8 kcal mole$^{-1}$), and cyclopentane and cyclohexane[26] (793.6 and 944.5 kcal mole$^{-1}$) lead to strain energies per $CH_2$ group (9.2, 6.5, 1.3, and zero kcal, respectively) somewhat different from those which have previously been discussed.

These and other effects of angle strain can be discussed in terms of modern valence theory, although mainly from a semi-empirical and often speculative, rather than fundamental, viewpoint. We shall now review this discussion briefly, adding some new elements and consciously emphasizing those which appear to be most directly pertinent to the C−C distances, HCH angles, and strain energies.

Kilpatrick and Spitzer[27] have treated the cycloalkanes, taking the C−C bond strength proportional to the product of the angular parts of the bonding orbitals in the bond direction (whether or not the orbitals point in this direction) and varying the hybridization ratio to maximize the product for the bond angle required by the geometry of the molecule, and Förster[28] and Coulson and Moffitt[29,30] have made related but much more elaborate quantum-mechanical considerations. And we have made calculations following the procedure described by Kilpatrick and Spitzer, except that simultaneous variation of the energy contributions $E_{CC}$ and $E_{CH}$ has been taken into account[31] on the assumption that they are given by $E_{ij}=S_iS_jE_{ij}^0/(S_iS_j)_{\max}$, with $S_i$ the value of the angular part of the bonding orbital in the internuclear direction. For $E_{CC}^0$ and $E_{CH}^0$ we have rather arbitrarily used the values 57.6 and 87.3 kcal mole$^{-1}$.[32] These treatments lead to strain energies and HCH bond angles in rough agreement with the experimental values (Table II). Coulson and Moffitt,[30] furthermore, argue that the bond "bendings" which are involved may well lead to shortening of the C−C internuclear distances, but they have given no quantitative estimates of the effect. It appears that this argument might be expressed in terms of the significant existence of a bond line, to be distinguished from the internuclear (straight) line, which more or less follows a line of maximum density of the bonding electron dis-

TABLE I. Measured and calculated $q$ values.

| Max | Min | Curve $q_0$ | $B$ $q/q_0$ | $D$ $q/q_0$ | $E$ $q/q_0$ |
|---|---|---|---|---|---|
| | 1 | 7.60 | (1.039) | (1.053) | (1.053) |
| 1 | | 12.34 | (1.029) | (1.054) | (1.048) |
| | 2 | 15.31 | (0.980) | (0.947) | (0.947) |
| 2 | | 20.19 | (0.981) | (0.976) | (0.981) |
| | 3 | 23.75 | (1.021) | (1.019) | (1.021) |
| 3 | | 28.79 | 1.007 | 1.006 | 1.006 |
| | 4 | 33.89 | 1.012 | 1.008 | 1.009 |
| 4 | | 39.81 | 1.006 | 1.005 | 1.007 |
| | 5 | 42.78 | (1.017) | (1.028) | (1.028) |
| 5 | | 46.10 | (1.009) | (1.009) | (1.009) |
| | 6 | 49.74 | 1.005 | 1.003 | 1.008 |
| 6 | | 55.72 | 1.004 | 1.000 | 1.005 |
| | 7 | 60.91 | 1.009 | 1.008 | 1.006 |
| 7 | | 66.36 | 1.007 | 1.002 | 1.002 |
| | 8 | 72.05 | 1.001 | 0.999 | 0.999 |
| 8 | | 79.60 | 1.005 | 1.005 | 1.007 |
| | 9 | 86.84 | 1.008 | 1.005 | 1.008 |
| 9 | | 92.84 | 1.006 | 1.005 | 1.001 |
| | 10 | 99.59 | (0.996) | (0.995) | (0.994) |
| 10 | | 105.18 | (0.997) | (0.997) | (0.996) |
| Average, 11 features | | | 1.0064 | 1.0042 | 1.0053 |
| Average deviation | | | 0.0020 | 0.0023 | 0.0026 |

Scale factor: $\frac{1}{3}(1.0064+1.0042+1.0053)=1.0053$.

$C-C=1.56\times1.0053=1.56_8$A
$C-H=1.09\times1.0053=1.09_6$A

[18] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

[19] O. Bastiansen and O. Hassel, Tidsskr. Kemi Bergv. Met. **6**, 71 (1946). Dr. Bastiansen has informed us that 1.525 A is a more likely value on the basis of their work, in view of the exact position (1.535 A) of their radial distribution maximum and of a probable error of +0.6 percent in wavelength calibration.

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[30] C. A. Coulson and W. E. Moffitt, Phil. Mag. **40**, 7th series, 1 (1949).

[31] We are indebted to Professor Pauling for having drawn our attention to the improvement that can be obtained in this way.

[32] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York 1939).

TABLE II. Observed and calculated values of HCH angles and strain energies (in kcal $(CH_2\ mole)^{-1}$) for cyclopropane and cyclobutane.

| | Cyclopropane | | Cyclobutane | |
|---|---|---|---|---|
| | ∠HCH | Strain energy | ∠HCH | Strain energy |
| Observed | 118° (reference 19)<br>116° (reference 20) | 9.2 | 114° | 6.5 |
| Kilpatrick and Spitzer | 122° | 8 | 115½° | 2 |
| Coulson and Moffitt (reference 29) | 113° | ... | ... | ... |
| Coulson and Moffitt (reference 30) | 116° | ~12 | 111° | ... |
| Förster | 119½° | ~35 | 113½° | 6.4 |
| Dunitz and Schomaker | 117° | 7.0 | 113° | 1.1 |

tribution, and which, in the bent bond, tends to retain a fixed length, thereby possibly causing the internuclear distance to be shortened in spite of the resulting increased internuclear repulsion. The ends of this line would presumably be tangent to the directions of the two bonding orbitals. Indeed, Copley[33] and Bernstein[34] have drawn attention to the remarkable fact that if the central bonds of ethylene and acetylene are regarded as extreme cases of bent bonds (formed by two and three $sp^3$ bonds, respectively), the internuclear distances are related to the ethane value as chord and arc of a circle ($d=d_0 \sin\theta/\theta$, where $\theta$ is the half-angle of strain). The agreement obtained for these extreme cases is surprising, but one could expect the relationship to hold for the comparatively small strain angles of the ring compounds, and Copley was able to show that it does hold for cyclopropane. Values obtained with this relationship, especially in slightly modified form, are in fact in good agreement (Table III) with the present experimental values, except, of course, for cyclobutane.

For Table III we have taken no account of any change in covalent radius which might occur purely as a result of rehybridization. Coulson's values of atomic radius as function of hybridization ratio[35] and Coulson and Moffitt's hybridization ratios[30] predict increases in C—C distance of about 0.01A for cyclobutane and 0.04A for cyclopropane. It is not clear whether this effect is really to be expected, and we shall ignore it in the remaining discussion. It may be noted, however, that the predicted magnitude is small enough to be essentially immaterial for cyclobutane and not out of the question for cyclopropane, since Table III need not be regarded as limiting for the amount of the characteristic bent bond shortening. For spiropentane, moreover, necessary retention of $sp^3$ hybridization at the central atom may well account for the shorter central bonds, by way of the absence of rehybridization change of radius or greater bent-bond shortening or both, while the forces due directly to the unequal effective bond angle strains must also contribute.

We believe that most of the lengthening of C—C bonds in four-membered rings, contrasted with the slight shortening to be expected from the bent bond concept, may well be an altogether different kind of effect, due to repulsion of nonbonded carbon atoms. The cross-ring distance in cyclobutane is only 2.22A and interaction of the non-bonded atoms may therefore be expected to be of some significance. In cyclopropane, on the other hand, each carbon atom is bonded to both others so that no interaction of this type exists; in cyclopentane, with the C—C—C angle close to tetrahedral, the interactions would be comparatively small although there are twice as many per $CH_2$ group as in cyclobutane.

Support for the existence of such a potential is given by the strain energies of the cycloalkanes if the magnitudes of the valence deformation energies are correctly indicated by Kilpatrick and Spitzer's, Coulson and Moffitt's, and our calculations, rather than by Förster's. This is illustrated by Fig. 2 (based on our calculation, which, we feel, may provide the best working formula in spite of its obvious deficiencies); with suitable corrections for torsional strain, good agreement is obtained for cyclopentane and cyclopropane but cyclobutane is 3.4 kcal $(CH_2\ mole)^{-1}$ more unstable than expected. Attributing this difference to repulsion of nonbonded carbon atoms we obtain $V_{C\cdots C}=6.8$ kcal mole$^{-1}$. Moreover, the force constant for CCC bond bending (dotted curve) is very much greater than would follow from valence deformation (full curve) alone and the difference can be attributed to a C···C repulsion representable by a quadratic potential with minimum at 109½° and amounting to about 5.4 kcal mole$^{-1}$ at 90°, in good agreement with the previous estimate.[36]

These values for the nonbond potential are in

TABLE III. Bond distances calculated with the relationship $d=1.542 \sin\theta/\theta$.[a]

| | $\theta$ | $d$ | $\theta'$ | $d'$ |
|---|---|---|---|---|
| Ethylene | 54°44′ | 1.318 | 50° | 1.353 |
| Acetylene | 70°32′ | 1.181 | ... | ... |
| Cyclopropane | 24°44′ | 1.495 | 22° | 1.504 |
| Cyclobutane | 9°44′ | 1.535 | 9° | 1.535 |

[a] The effective half-angle of strain $\theta'$ is given as corrected for rehybridization by Coulson and Moffitt (see reference 30).

[33] C. N. Copley, Chem. and Ind. 663 (1941).
[34] H. J. Bernstein, J. Chem. Phys. **15**, 284 (1947).
[35] C. A. Coulson, Victor Henri Commemorative volume, *Contribution à l'Étude de la Structure Moléculaire* (Desoer, Liège, 1948), p. 15.

[36] That repulsive forces between nonbonded heavy atoms are not negligible compared with bond stretching or bond bending forces has been demonstrated by T. Simanouti, J. Chem. Phys. **17**, 245, 734, 858 (1949). See also J. W. Linnett and D. F. Heath J. Chem. Phys. **19**, 801 (1940); Trans. Faraday Soc. **44**, 873, 878, 884 (1948); **45**, 264 (1949). Although it has been inferred that the nonbonded H···H force constants in methane are negligibly small, Mulliken, in his recent treatment (reference 38) of bond energies, is led to expect them to be considerable. Moreover, a Kilpatrick, Spitzer, and Pauling calculation of the contribution of valence deformation to the force constants for methane leads to a very much too small value of the HCH bending constant, even though the observed vibrational potential function can be nicely represented as a pure-stretching, pure-bending function without interaction terms.

rough accordance with Pauling's relationship[37] $-\Delta R(n) = 0.353 \log n$, which may be assumed to apply, at least for order of magnitude, to antibonding as well as bonding; for $\Delta R \sim 0.34$ (i.e., $(2.22-1.54)/2$) the relationship gives a bond number $n$ of about 0.1, as would correspond in the case of bonding to an energy of about 6 kcal mole$^{-1}$. For $\Delta R(n) \sim 0.5$ (tetrahedral CCC angle), the corresponding $n$ is about 0.04. Examination of the variation of Mulliken's overlap integrals[38] with interatomic distance shows that they also would lead to the same order of magnitude for the nonbond interaction.

We now estimate the stretching of the C—C bonds in cyclobutane due to C···C repulsion, by expressing the energy of the symmetrical molecule as

$$V(r_{CC}) = V_0 + k_1(R^0_{C\ldots C} - \sqrt{2} r_{CC})^2 + 2k_2(r_{CC} - r_{CC}^0)^2.$$

Here $R^0_{C\ldots C}$ is the C···C distance for tetrahedral angle (2.52A), $r_{CC}^0$ is 1.54A, and $k_1$ and $k_2$ are respectively the force constants for C···C repulsion and C—C stretching. The equilibrium condition is then

$$(r_{CC} - r_{CC}^0) = \frac{R^0_{C\ldots C} - \sqrt{2} r_{CC}^0}{\sqrt{2}} \cdot \frac{k_1}{k_1 + k_2} = \frac{0.34}{\sqrt{2}} \cdot \frac{k_1}{k_1 + k_2},$$

which on the assumption of $k_1 = 133$ kcal mole$^{-1}$ $A^{-2}$ (from $2V_1 = 12 = k_1(0.30)^2$) and $k_2 = 5 \times 10^5$ erg cm$^{-2}$ $= 715$ kcal mole$^{-1}$ $A^{-2}$ gives $(r_{CC} - r_{CC}^0) = 0.038$ A, in pleasing agreement with the observed lengthening.

Following the above discussion the potential energy per $CH_2$ group as function of the dihedral angle of puckering can be expressed as

$$V' = V_0' - 2V_1'(1 - \cos 3\phi) + 4V_2'(\theta) + k_1[R^0_{C\ldots C} - R_{C\ldots C}]^2,$$

where $V_1'$ is the torsional potential barrier,[39] $\phi$ the torsional angle, $4V_2'(\theta)$ the valence deformation energy corresponding to the CCC angle strain, and $k_1$ the repulsion force constant previously introduced. We find that the balance of these terms is so delicate at small dihedral angles as to make it impossible to predict whether the equilibrium configuration of the ring is planar or slightly nonplanar, and we await the results of future spectroscopic work with great interest. It may be noted that the total potential energy associated with the C—C torsions would presumably be a decreasing function of $r_{CC}$, at least for the opposed orientation, and so might contribute to the apparent stretching of C—C as discussed above, especially in the preceding paragraph. This effect is probably negligible, however, since cyclopentane, with its quite small bond-angle strains, shows normal or possibly even slightly shortened C—C distances, in spite of the predominantly opposed orientations[39] (see also the reference in the legend to Fig. 2) about the C—C bonds.

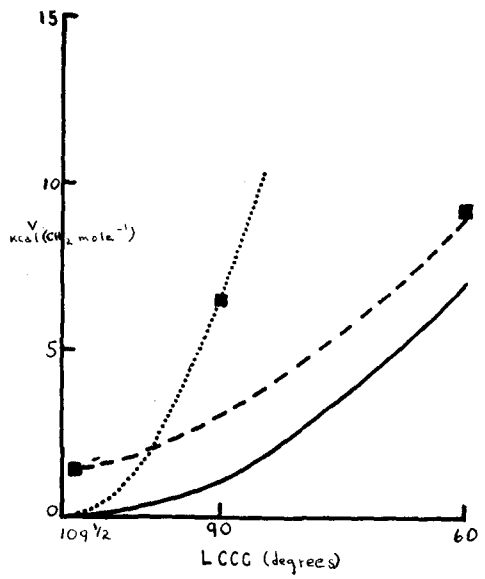


FIG. 2. Observed strain energies (in kcal ($CH_2$ mole)$^{-1}$) for cyclopropane, cyclobutane, and cyclopentane. Full curve: calculated valence deformation energy as function of CCC angle. Dashed curve: calculated valence deformation energy (full curve) plus estimated correction for torsional strain energy caused by opposition of adjacent $CH_2$ groups (see reference 39), of 2 kcal mole$^{-1}$ for cyclopropane and cyclobutane and 1.3 kcal mole$^{-1}$ (the total strain energy) for cyclopentane. The lower value for cyclopentane is appropriate because of ring puckering. Dotted curve: the quadratic potential $V = \frac{1}{2}k(\Delta\theta)^2$ with $k = 8 \times 10^{-12}$ radian$^{-2} = 35$ cal mole$^{-1}$ degree$^{-2}$ (Kilpatrick, Pitzer, and Spitzer, J. Am. Chem. Soc. **69**, 2683 (1947)).

[37] L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947).
[38] R. S. Mulliken, J. Am. Chem. Soc. **72**, 4493 (1950).
[39] See K. S. Pitzer, Science **101**, 672 (1945).